NEWARK PUBLIC LIBRARY

OCT 6 1982

U. S. GOVT. PUBS.
DEPOSITORY 376

RI 8690

Bureau of Mines Report of Investigations/1982

Recovery of Zinc and Sulfur From Sphalerite Concentrates by Reaction With Sulfuric Acid

By H. H. Dewing, S. E. Lay,
and A. A. Cochran

UNITED STATES DEPARTMENT OF THE INTERIOR

I 28.23:

Report of Investigations 8690

Recovery of Zinc and Sulfur From Sphalerite Concentrates by Reaction With Sulfuric Acid

By H. H. Dewing, S. E. Lay,
and A. A. Cochran

UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
Robert C. Horton, Director

This publication has been cataloged as follows:

Dewing, H. H. (H. Harvey)

Recovery of zinc and sulfur from sphalerite concentrates by reaction with sulfuric acid.

(Bureau of Mines report of investigations ; 8690).

Bibliography: p. 15.

Supt. of Docs. no.: I 28.23:8690.

1. Zinc—Metallurgy. 2. Sulphur. 3. Sphalerite. 4. Sulphuric acid. I. Lay, S. E. (Scott E.). II. Cochran, A. A. (Andrew A). III. Title. IV. Series: Report of investigations (United States. Bureau of Mines) ; 8690.

TN23.U43 [TN796] 622s [669'.52] 82-600177 AACR2

CONTENTS

	Page
Abstract	1
Introduction	1
Pyrometallurgical processes	2
The U.S. zinc industry	2
Previous hydrometallurgical research	2
Reaction with H_2SO_4	2
Design and construction of PRU	3
Scale-up criteria	4
Three-stage reactor design	4
Materials and construction	5
Separation of reactor products	6
Controls and operation	8
Safety equipment and procedures	9
PRU feed materials	9
Sulfuric acid	9
Sphalerite concentrate	9
Results of PRU operation	10
Feed rates	10
Reaction products	10
Leaching and crystallization of zinc sulfate	12
Projections to larger scale operation	13
Summary	14
References	15
Appendix.--Procedure for rapid in-plant assay of sulfuric acid solutions	16

ILLUSTRATIONS

1.	Process flowsheet for recovery of zinc and sulfur from sphalerite by reaction with sulfuric acid	3
2.	Three-stage reactor system for reaction of sphalerite with sulfuric acid.	4
3.	Bottom view of PRU showing control panel, settling reactor, and gas scrubber	6
4.	Upper view of PRU showing ore feeder, premix reactor, and stirred reactor	7
5.	Upper view of PRU showing top of settling reactor and stirred reactor	8
6.	Solubility of zinc sulfate in sulfuric acid solutions and crystallization lines for zinc sulfate heptahydrate formation	13
A-1.	Determination of H_2SO_4 concentration by in-plant assay method	16

TABLES

1.	Three-stage reactor system design	5
2.	Chemical analysis of ZnS concentrate	9
3.	Analyses of representative product samples from the PRU	11
4.	PRU test conditions and zinc recoveries	11
5.	Analysis of potentially hazardous leach residue	12
6.	Concentration of crystallizer solutions	13

RECOVERY OF ZINC AND SULFUR FROM SPHALERITE CONCENTRATES BY REACTION WITH SULFURIC ACID

By H. H. Dewing,[1] S. E. Loy,[2] and A. A. Cochran[3]

ABSTRACT

The Bureau of Mines constructed a process research unit (PRU) to demonstrate new technology for extracting zinc from sphalerite concentrates. Up to 9 kg/hr of sphalerite (ZnS) concentrate was reacted at ambient pressure in the PRU with 80 pct sulfuric acid at 160° to 180° C to produce zinc sulfate and elemental sulfur. The PRU consisted of a three-stage glass reactor system: a 4-liter premix stage in which feed was slurried with 78 to 82 pct H_2SO_4, a 40-liter stirred reactor, and a 150-liter settling stage in which high reaction conversions were effected and excess H_2SO_4 for recycle was separated from insoluble $ZnSO_4$ and sulfur. Evolution of sulfur-containing gases was minimized by subsurface addition of acid feed slurry to the stirred reactor and by exclusion of air from the reactor to prevent the oxidation of elemental sulfur. Conversion of zinc to zinc sulfate averaged over 99 pct at the optimum acid concentration of 80 pct. Total sulfur losses (primarily SO_2) were less than 2 pct of the sulfur in the sphalerite. Elemental sulfur remained in the insoluble portion of the settled reactor product after leaching with simulated spent zinc electrolyte containing sulfuric acid. The sulfur residue contained 75 to 89 pct sulfur. Neutral zinc sulfate, required for zinc electrowinning processes, was separated from the sulfuric acid leach solution by crystallization at -15° C as zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$). The crystallization operation simultaneously effected a partial concentration of the recycled electrolyte solution by removing water.

INTRODUCTION

This research was conducted by the Bureau of Mines in support of its overall goals of helping to maintain an adequate supply of minerals and metals for future national needs with minimum waste of resources and degradation of the environment. The objective of the current investigation was to demonstrate, at larger than bench scale, a hydrometallurgical method for recovering zinc from ZnS concentrates while avoiding the formation of toxic H_2S and SO_2 gases. The results of earlier laboratory investigations were used to design a process research unit (PRU) for continuous steady-state processing tests at rates up to 9 kg/hr of ZnS.

[1]Research chemist, Rolla Research Center, Bureau of Mines, Rolla, Mo.
[2]Physical science technician, Rolla Research Center, Bureau of Mines, Rolla, Mo.
[3]Supervisory research chemist, Rolla Research Center, Bureau of Mines, Rolla, Mo.

Pyrometallurgical Processes

Most currently employed methods for commercial zinc production rely on smelter roasting of ZnS concentrates and first came into widespread usage in the early 19th century. The calcine produced by the roaster may be converted into metallic zinc by various processes (7).[4] The early retort processes have now been largely supplanted by electrowinning from calcine leach solutions. Still, sulfur dioxide gas produced by roasting the ZnS remains an undesirable byproduct of zinc production. Although this SO_2 is usually converted to sulfuric acid, the acid is not always a profitable byproduct because of the high costs of production from dilute, hot, dusty SO_2 gas streams and because of excess supplies of the acid in some geographical areas.

In contrast, if the sulfur byproduct is recovered in the solid, elemental form, it can be easily stored or shipped and is appreciably more versatile than either the SO_2 gas or the sulfuric acid.

The U.S. Zinc Industry

The 1970's were a trying decade for the U.S. zinc industry. In the early part of the decade, because of continuing and worsening economic and environmental problems, a number of older zinc smelters were shut down. The single zinc production facility built in the decade was the first new facility to be built in the United States in 37 years. The U.S. share of world zinc production has declined from 24 pct in 1963 to 9 pct in 1980, and nearly 60 pct of the domestic demand for primary zinc now must be supplied by imports from foreign zinc producers (1). Yet the United States and North America have some of the largest known reserves of zinc in the world (9). To decrease the dependence of U.S. zinc consumers on foreign suppliers, new technology in the form of efficient, economical, and nonpolluting procedures is needed.

Previous Hydrometallurgical Research

Numerous investigations have been reported on direct leaching of ZnS in H_2SO_4 solutions and the similar problem of leaching iron sulfides (3-4, 6). For the most part, the results have shown that the final oxidation state of sulfur is quite variable. The oxidation state of the sulfur and the rate of reaction are dependent in a complex way on the oxidizing conditions, the acid concentration, and the impurities in the metal sulfide. The reaction occurs in several stages with H_2S gas and elemental sulfur being formed first, followed by SO_2 gas and sulfuric acid. In the absence of oxygen overpressure, H_2S is produced, which may be followed by further oxidation to elemental sulfur either homogeneously or heterogeneously on the surface of the ZnS. At low temperatures, Forward observed that sulfur formed in solid pellets and occluded some of the reactant materials (5). The rate of reaction was notably faster for impure natural sphalerite than for synthetic sphalerite. Stanczyk and Rampacek studied the effect of adding of iron sulfides to the reaction system (8). The work described herein differs from these studies in that strong acid was used at ambient pressure and zinc sulfate product remained undissolved.

Reaction With H_2SO_4

In earlier reported bench-scale research at the Rolla Research Center, ZnS was reacted with moderately concentrated (~80 pct) H_2SO_4 at atmospheric pressure to produce elemental sulfur and zinc sulfate (2). A simplified flowsheet of the procedure used to separate and recover zinc and sulfur from the reaction products is shown in figure 1. In the reaction of ZnS with sulfuric acid, the

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

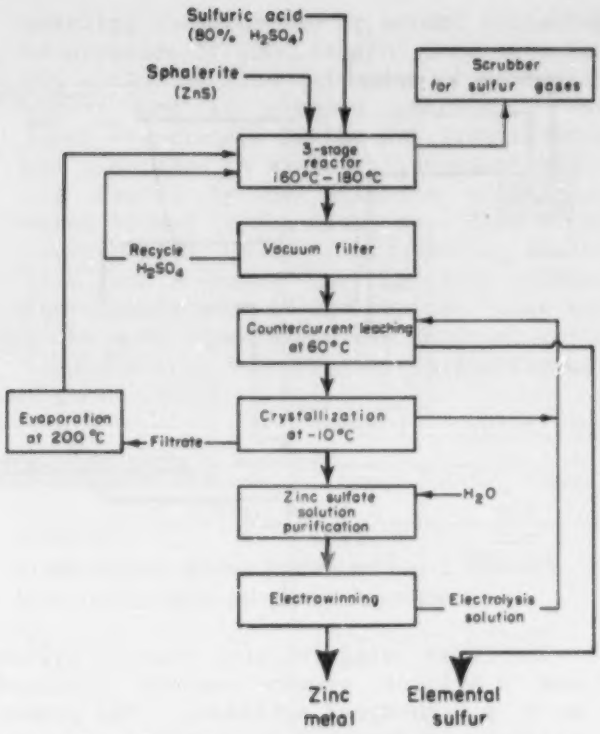

FIGURE 1. - Process flowsheet for recovery of zinc and sulfur from sphalerite by reaction with sulfuric acid.

sulfuric acid solution was used to generate a pseudohomogeneous reaction medium in which the final oxidation state of the converted sulfur could be easily controlled.

More concentrated (>80 pct) H_2SO_4 reacted with the ZnS to produce SO_2 gas:

$$ZnS + 4H_2SO_4 \rightarrow ZnSO_4 + 4SO_2 + 4H_2O. \quad (1)$$

Moderately concentrated H_2SO_4 (~80 pct) reacted with the ZnS to produce elemental sulfur:

$$3ZnS + 4H_2SO_4 \rightarrow 3ZnSO_4 + 4S^\circ + 4H_2O. \quad (2)$$

More dilute (<80 pct) H_2SO_4 reacted with the ZnS to produce H_2S gas:

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S. \quad (3)$$

When the H_2SO_4 solution was at the optimum concentration for formation of sulfur, the formation of both SO_2 and H_2S was practically eliminated. The reaction temperature range was 170° to 200° C, but reaction temperatures did not have a large effect on quantity or kind of sulfur gases formed.

This research also indicated that elemental sulfur could be formed in the reaction process from several other auxiliary reactions when conditions were conducive. Some H_2S gas formed from the initial reaction of ZnS with H_2SO_4 and was swept out by the CO_2 gas produced by the reaction of the acid and carbonate minerals. But H_2S gas reacted rapidly with the moderately concentrated H_2SO_4 to produce sulfur:

$$H_2SO_4 + 3H_2S \rightarrow 4S^\circ + 4H_2O. \quad (4)$$

A second sulfur-forming reaction was observed when H_2S gas reacted with SO_2 gas:

$$SO_2 + 2H_2S \rightarrow 3S^\circ + 2H_2O. \quad (5)$$

DESIGN AND CONSTRUCTION OF PRU

After laboratory tests showed the feasibility of the reaction of ZnS with moderately concentrated H_2SO_4 in batch tests, tests under steady-state continuous operation conditions were needed. A PRU with larger scale equipment for continuous operation was designed to prove the feasibility of the reaction scheme under operating conditions similar to potential commercial development. Results from the operation of the PRU were to be used to provide information not available from laboratory tests on the steady-state operation and data for further process evaluation.

Scale-Up Criteria

Four main criteria were judged to be important to the efficiency of the reaction process:

1. Maintain the reaction conditions necessary to achieve maximum conversion of ZnS to $ZnSO_4$.

2. Minimize residence time of reactants in the reactor and the size of the reactor.

3. Minimize the evolution of sulfur gases.

4. Provide other conditions to promote the formation of elemental sulfur from sulfur gases formed by undesirable reactions.

A steady-state stirred reactor operating at constant temperature and acid concentrations provides the best conditions for minimizing evolution of sulfur-containing gas. However, the desired reaction of ZnS with H_2SO_4 follows first-order reaction kinetics (2), and such a reactor cannot be efficiently used to obtain high conversions for first-order reactions. Plug flow reactor designs offer about 10 times greater volumetric efficiency for first-order reactions at 99-pct conversion. The plug flow reactor also does not require mixing power, which is an important factor as the formation of liquid elemental sulfur in the reaction creates a very viscous mixture. However, the plug flow reactor does not lend itself to the maintenance and control of optimum reaction conditions necessary to minimize the evolution of sulfur-containing gases.

Three-Stage Reactor Design

A three-stage reactor system was designed to obtain maximum conversion of ZnS and to minimize sulfur gas evolution. Figure 2 shows a schematic of the reaction system.

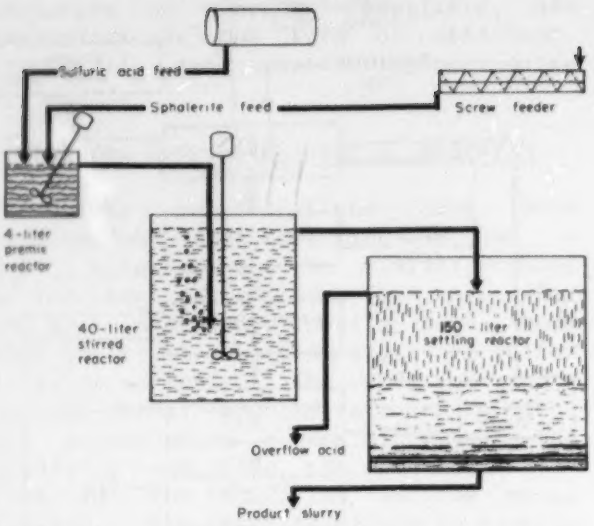

FIGURE 2. - Three-stage reactor system for reaction of sphalerite with sulfuric acid.

The first stage of the reactor system was a 4-liter premix reactor equipped with a high-speed agitator. The premix reactor was operated at ambient temperature. The finely ground sphalerite concentrate was slurried with sulfuric acid feed, and any residual carbonates or other reactive materials in the concentrate react with the acid. The reaction of ZnS to produce H_2S gas is negligible at this temperature.

The second-stage reactor was a 40-liter stirred reactor with a normal operating temperature of 175° to 190° C. The slurried feed mixture from the premix reactor was fed to the stirred reactor through a dip tube extending about 18 inches below the solution level in the reactor. Under these conditions, H_2S gas evolution was insignificant, as laboratory tests showed that over 99 pct of the H_2S gas formed by the initial rapid reaction of the ZnS with hot acid was converted to elemental sulfur before it reached the surface.

The overflow from the stirred reactor after an average residence time of 30 to 45 min was received by the 150-liter third-stage settling reactor. The

READEX FICHE best copy available

settling reactor had a normal operating temperature of 150° to 170° C to minimize SO_2 evolution from oxidation of elemental sulfur and to promote settling. The lower temperature in the settling reactor was also used to minimize transient boiling caused by the dilution effect of water formed in the reaction. This transient boiling causes increased SO_2 evolution and disrupts the settling action. The temperature in the reactor also had to be maintained below the point at which liquid sulfur becomes extremely viscous; otherwise, the viscous sulfur entrained gases and did not settle with the other insoluble reaction products. Zinc sulfate, which is insoluble in the sulfuric acid, settled in the reactor along with sulfur and insoluble gangue and was withdrawn from the bottom of the reactor as a thick slurry after a residence time of 3 or more hours. Sulfuric acid for recycle was removed from the top of the settling reactor by overflow. The reactor design factors are given in table 1.

TABLE 1. - Three-stage reactor system design

Stage	Volume, liters	Temp, ° C	H_2SO_4 conc., pct	Function	Process effect
Premix reactor.	4	Ambient	80+	Slurries ZnS with H_2SO_4.	Removes CO_2 gas; produces slurry feed.
Stirred reactor.	40	170-190	75-80	1. Initiates ZnS reaction. 2. Minimizes H_2S gas evolution.	1. Converts 50+ pct of ZnS to $ZnSO_4$. 2. Reacts H_2S and SO_2 with H_2SO_4 to produce S°.
Settling reactor.	150	150-170	65-75	1. Reacts ZnS to completion. 2. Separates solids from excess H_2SO_4. 3. Minimizes SO_2 gas formation.	1. Converts up to 100 pct of ZnS to $ZnSO_4$. 2. Produces H_2SO_4 for recycle. 3. Produces product slurry.

The reactor system was sealed from the atmosphere, and gaseous effluents were exhausted through overhead piping. A gas burner in the exhaust stream was used to burn any H_2S gas, and a sodium carbonate scrubber was used to absorb SO_2 gas.

Materials and Construction

In the construction of the PRU, one major requirement was that no stainless steels, nickel alloys, or exotic metals could be used. Nickel and cobalt and some of the exotic metals are quite deleterious to conventional zinc electrowinning processes, and thus even minimal corrosion would have severely contaminated the zinc sulfate product.

Views of the PRU are shown in figures 3, 4, and 5. The reactors and associated piping were constructed from thermal-shock-resistant glass with polytetrafluoro ethylene (PTFE) gaskets, seals, agitators, and valves. Lead-pipe heat exchanger coils were used to cool the hot acid effluents from the reactors. Feed acid and cooled acid solutions were transported by cross-linked polyvinyl chloride (CPVC) pipes, polypropylene and polyethylene vessels, and pumps made of CPVC, polypropylene, and Viton.[5]

[5]Reference to trade names is for identification only and does not imply endorsement by the Bureau of Mines.

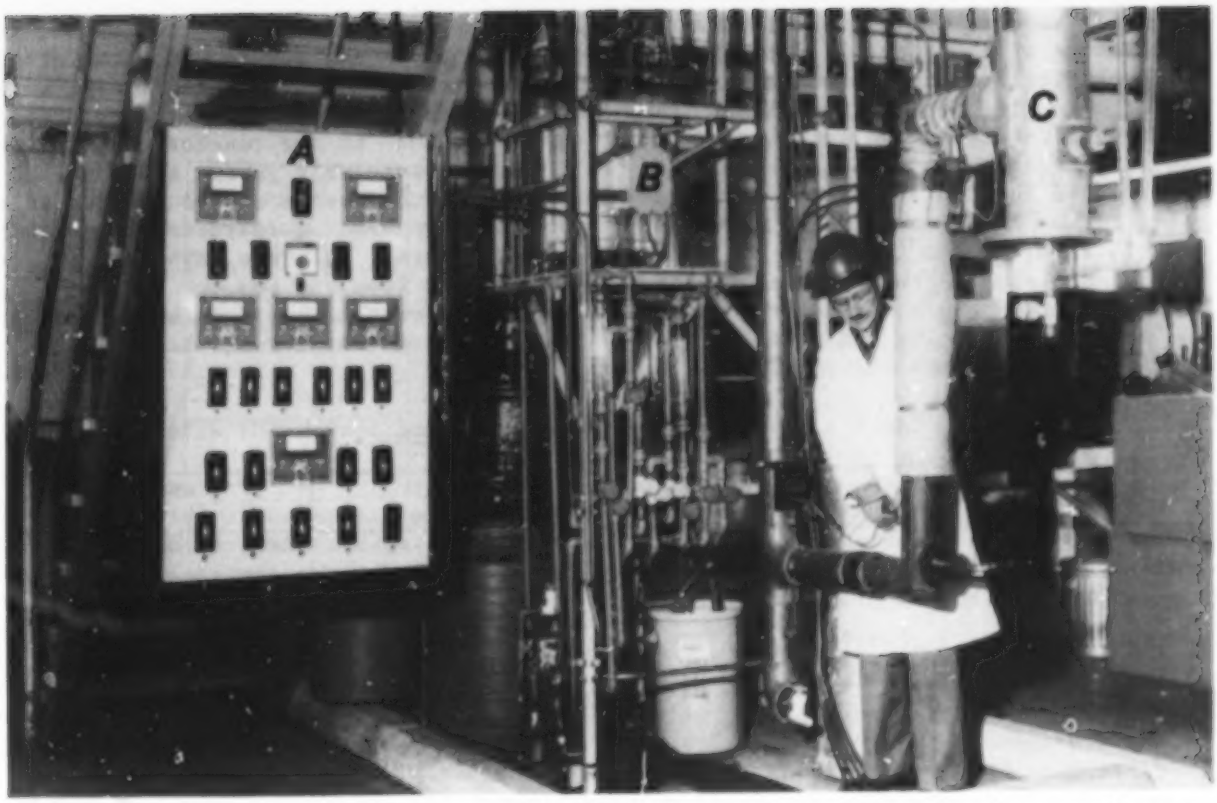

FIGURE 3. - Bottom view of PRU showing control panel (*A*), settling reactor (*B*), and gas scrubber (*C*).

The reactor vessels were supported on a 20-ft-high support structure of 1-1/2-inch PVC-coated pipe and were shielded by clear acrylic plastic sheets. Access to the reactors for maintenance and feeding was provided by an elevated platform surrounding the support structure. After feed acid was pumped to the premix reactor, gravity was used to move the hot reactants through the reactor system.

Separation of Reactor Products

The reactor product slurry contained $ZnSO_4$, elemental sulfur, gangue material, and up to 40 pct unreacted H_2SO_4. A tilting-pan vacuum filter with duplex 2- by 2-ft pans was used to separate a portion of the excess acid from the solids. Vacuum power for the filter was supplied by a water-sealed centrifugal vacuum pump. Sulfuric acid filtrate was pumped from the receiver tank to recycle storage.

The filter cake produced by the filter was leached by countercurrent decantation with simulated zinc electrolyte in a series of four 30-gal mixer-settler tanks. This operation produced a saturated solution of $ZnSO_4$ and an insoluble residue of elemental sulfur and gangue. The leach solution was filtered and stored for use as feed solution to the crystallizer.

The crystallizer system was designed to separate $ZnSO_4$ from the acid leach solution by crystallization of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) at -15° C. Two 30-gal tanks were insulated with 3 inches of vermiculite, with one serving as the crystal receiver and accumulator and the other as the refrigeration heat transfer tank. Leach solution feed was continuously added to the crystal accumulator and recirculated through the refrigeration heat transfer tank to maintain the desired operating temperature. A 100-ft coil of 1/2-inch copper tubing was used in the agitated refrigeration tank to

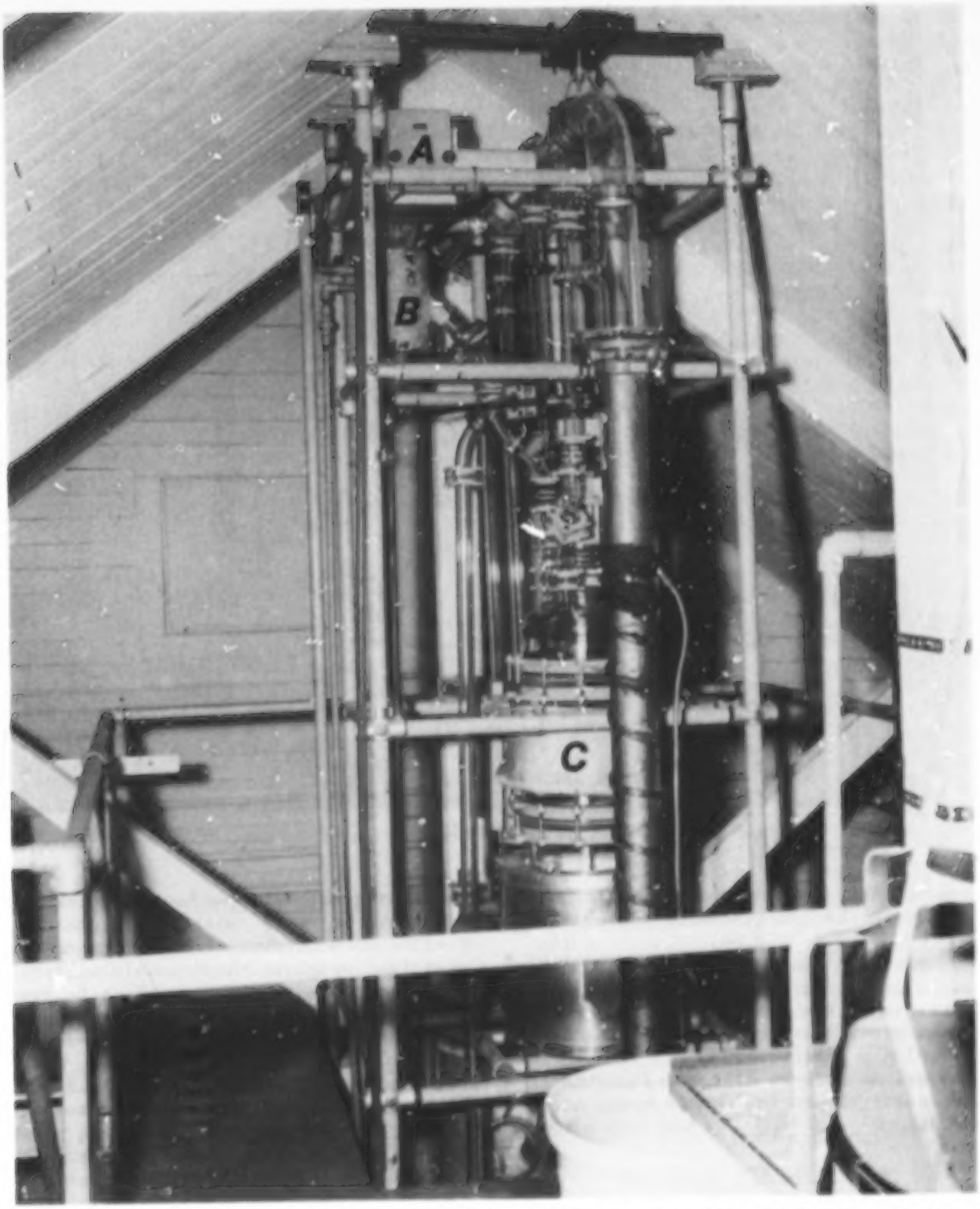

FIGURE 4. - Upper view of PRU showing ore feeder (*A*), premix reactor (*B*), and stirred reactor (*C*).

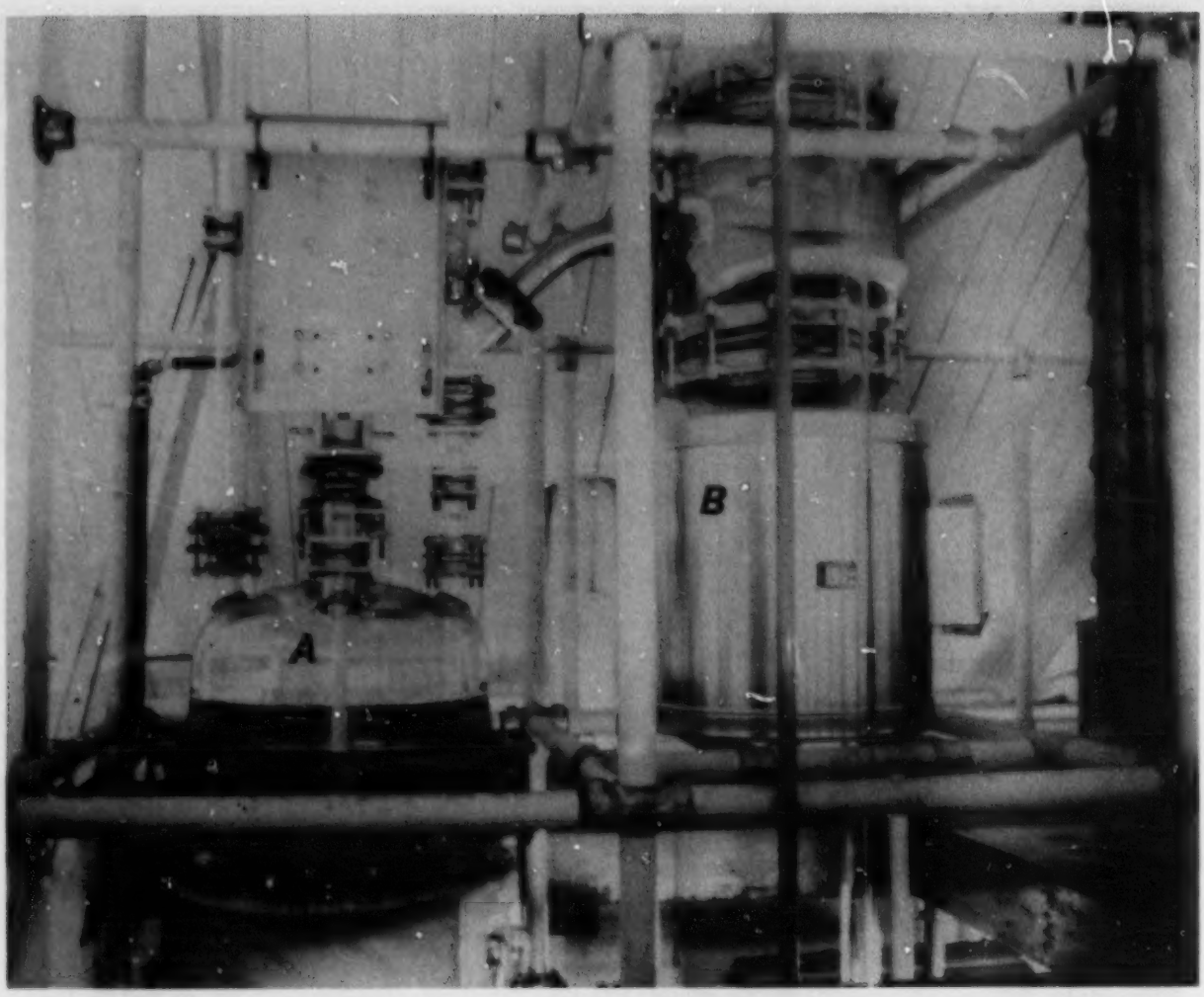

FIGURE 5. - Upper view of PRU showing top of settling reactor (*A*) and stirred reactor (*B*).

remove heat, and power was supplied by a 36,000-Btu/hr refrigeration system.

The crystals of $ZnSO_4 \cdot 7H_2O$ had a specific gravity of 1.96 and were allowed to settle out from the crystal liquor (specific gravity about 1.5) in the unagitated accumulator tank. They were removed as a dense slurry and washed free of acid by elution with zinc sulfate solution.

Controls and Operation

Each reactor was heated with large electrical resistance heating mantles containing multiple independent elements. Temperatures were monitored and controlled with Chromel-Alumel thermocouples contained by glass thermocouple wells and connected to controllers. About 5 hr was required to bring the reactors up to operating temperature.

The acid feed rate was controlled manually with ball-in-tube flowmeters. The sphalerite was metered into the premix reactor with a twin-screw feeder controlled by a variable-speed silicon-controlled rectifier (SCR) controlled dc motor.

The exhaust gases at several points in the system were periodically analyzed during test runs using a gas chromatograph connected in-line. To obtain actual evolution rates, a known flow rate of nitrogen was injected into the exhaust gas stream as a diluent, and analyses were made on upstream and downstream exhaust gases. This procedure was not completely reliable, so the scrubber solutions were analyzed for sulfur after the test to provide an average aggregate sulfur gas evolution rate for each test.

Safety Equipment and Procedures

Operation of the PRU with strong, hot H_2SO_4 involves considerable potential danger. From very early in the design process, factors to increase the operational safety were considered and incorporated into the design. The worst-case accident of a hot acid spill was considered in providing plastic sheathing around the entire reactor system. A flood dam was constructed from concrete parking lot wheel stops to contain hot acid spills in a small floor area.

An automatic H_2S monitor and alarm system provided continuous monitoring of the atmosphere and was supplemented by hand-operated gas monitors. An auxiliary gasoline-powered generator was available to power the exhaust blower and gas control equipment.

Other personnel protection equipment included plastic coveralls, rubber boots, face shields, water spray hoses, and an open barrel of dilute sodium carbonate solution for emergency neutralization of acid.

PRU FEED MATERIALS

Sulfuric Acid

Sulfuric acid used in the PRU tests was prepared by mixing commercial-grade concentrated acid with water and recycled acid to obtain the desired acid concentration. All strong acid solutions used in the PRU operation were assayed at the site by a heat-of-dilution method developed to provide rapid assays. The accuracy of the method is ±0.3 pct. (See appendix.)

Sphalerite Concentrate

The sphalerite (ZnS) feed for the PRU tests was a typical Missouri ZnS concentrate. A 5-ton supply of the concentrate was purchased after it had been preleached in normal operations at the AMAX zinc plant at Sauget, Ill. The preleaching step is used by several zinc smelters to remove magnesium from ZnS concentrates recovered from dolomitic deposits. The preleached concentrate was chosen as the PRU test material to minimize the amount of H_2S evolved with the CO_2 released on contact with acid. The analysis of the concentrate is given in table 2.

TABLE 2. - Chemical analysis of ZnS concentrate[1]

Element	Pct	Element	Pct
Zinc.....	58.8	Silicon.....	0.36
Sulfur.....	31.0	Copper.....	.19
Iron.....	1.42	Magnesium...	.10
Calcium.....	1.26	Cobalt.....	.05
Lead.....	1.24	Nickel.....	.03
Cadmium.....	.64		

[1]Balance mostly oxygen.

As received, the concentrate contained about 10 pct moisture and numerous limestone rock fragments. Before being used as PRU feed material, the concentrate was dried in ovens at 110° C and screened to remove the rock.

RESULTS OF PRU OPERATION

Feed Rates

The PRU was operated for test runs of 24-hr duration. The maximum feed rate of concentrate in steady-state operation was about 9 kg/hr, which required about 500 cm^3/min of acid feed to maintain good fluidity in the stirred reactor. This was the maximum feed rate of acid that could be maintained at steady-state temperature, unless the acid was preheated.

The lower feed rates used in our tests increased the residence time of the reactants in the stirred reactor. Also, the increased residence time increased the amount of conversion of ZnS to elemental sulfur in the stirred reactor. Under these test conditions, the additional liquid sulfur formed in the stirred reactor increased the viscosity of the reactor contents, and four to five times the stoichiometric amount of H_2SO_4 to ZnS required for reaction had to be used to maintain fluidity in the stirred reactor.

If it had been possible to increase the acid feed rate with additional heating capacity or to feed preheated acid, then the sphalerite feed throughput, or operating efficiency of the PRU reactor system, could have been improved. This improvement would have resulted from both an increase in total feed throughput and a decrease in the H_2SO_4-to-ZnS ratio needed to maintain fluidity in the stirred reactor, because less sulfur would be present. Optimum operating conditions requiring higher feed throughput would have decreased the residence time of the reactants in the stirred reactor and caused more of the elemental sulfur to have been formed after the reaction mixture was in the settling reactor. The probable results of these changes in operating conditions would have been a decrease in the H_2SO_4-to-ZnS ratio to about three times the stoichiometric ratio and greater overall efficiency.

Reaction Products

Sulfur in the ZnS feed was almost completely converted to elemental sulfur. Analysis of the scrubber solutions for each test showed that less than 2 pct of the sulfur feed was evolved as sulfur gases. The sulfur gases evolved were mostly SO_2 and only negligible amounts of H_2S. During operation of the PRU, a measurable concentration (greater than 1 ppm) of H_2S or SO_2 was never observed in the building containing the PRU. However, not all of the converted sulfur was recovered with the product slurry from the settling reactor. A portion of the sulfur floated in the settling reactor, presumably owing to gas entrapment, and overflowed with the recovered acid. This sulfur proved to be a problem when the overflow acid was cooled because it condensed into globules that were difficult to handle. The sulfur float problem was largely solved by decreasing the temperature in the settling reactor.

Product slurry was usually removed from the settling reactor at regular intervals so as to maintain a relatively clear H_2SO_4 overflow stream. The slurry was quenched in a cooled tank containing an accumulation of the product. The product slurry retained good fluidity after quenching, and there was no tendency to agglomerate or form lumps. Any very small lumps that formed were extremely friable owing to the large amounts of anhydrous zinc sulfate present.

Small samples of the slurry product were treated by dissolving the soluble portion (primarily zinc sulfate and sulfuric acid) in water and analyzing both the solid and liquid fractions after analytical separation. Representative sample analyses of the product are given in table 3. Table 4 shows the test conditions and zinc recoveries in the product as soluble zinc sulfate.

TABLE 3. - Analyses of representative product samples from the PRU

Test	Elapsed time,[1] hr	Product analysis, wt-pct[2]							Elemental sulfur in residue, pct
		Water-soluble component			Insoluble component				
		$ZnSO_4$	H_2SO_4	Iron	ZnS	S°	Iron	Other	
3.....	5.0	24.4	35.4	0.21	0.37	18.4	0.46	1.80	87.4
3.....	6.0	26.5	33.0	.24	.32	15.7	.38	1.40	88.2
5.....	12.0	30.0	34.7	.53	.04	8.5	.14	1.45	83.9
5.....	14.0	33.6	39.9	.21	.04	4.0	.04	1.23	75.4
6.....	8.0	36.2	40.2	.23	.41	4.6	.07	1.12	72.6
6.....	17.0	38.6	35.8	.23	.05	7.7	.09	1.16	84.0
8.....	7.0	35.7	41.0	.25	.46	4.2	.07	.81	75.8
8.....	15.0	33.6	43.1	.21	.04	7.6	.11	1.22	84.8
10.....	14.0	30.9	44.6	.20	.08	7.0	.08	1.53	80.7
10.....	16.0	35.8	38.5	.27	.02	8.6	.02	1.17	86.9
10.....	18.0	40.8	33.6	.31	.02	9.3	.02	1.23	87.3

[1]Measured from start of ZnS feeding.
[2]Balance mostly H_2O.

TABLE 4. - PRU test conditions and zinc recoveries[1]

Test	H_2SO_4 conc., pct	ZnS feed rate, kg/hr	Stirred reactor temp., ° C	Settling reactor temp., ° C	Elapsed run time,[2] hr	Zinc conversion, pct	Sulfur recovery, pct
3.....	78.0	9	170	160-165	5.0	97.5	([3])
					6.0	98.0	([3])
5.....	80.0	7-9	180	175	12.0	99.8	([3])
					14.0	99.8	42.6
6.....	78.0	7-9	180	175	8.0	98.1	45.1
					17.0	99.8	70.7
8.....	81.0	7	180	175	7.0	97.9	42.0
					15.0	99.8	80.5
10.....	81.0	7	180	160	14.0	99.6	81.2
					16.0	99.9	85.0
					18.0	99.9	80.7

[1]H_2SO_4 feed rate was 500 cm^3/min for all tests.
[2]Measured from start of ZnS feeding.
[3]Inaccurate samples.

There were no clear-cut relationships between product quality or zinc recoveries and the operating variables. The acid concentration had to be controlled within a narrow range of 78 to 82 pct to minimize sulfur gas formation, and observations indicate that the optimum acid concentration was probably about 80 pct. Virtually total conversion and recovery of the zinc as soluble zinc sulfate was achieved at all reactor operating temperatures tested. The critical variable determining reactor conversion of ZnS was confirmed to be the reactor residence time of the reactants. At the operating temperatures used in these tests, nearly total conversion was achieved with a residence time of about 4 hr.

The sample analyses showed that elemental sulfur recoveries in the product were less complete than zinc sulfate conversions. Based on the reaction stoichiometry (2) 4 moles of elemental sulfur are produced by the reaction for each 3 moles of zinc sulfate produced. Thus,

the concentration of elemental sulfur in the final product would equal 26.5 pct of the concentration of $ZnSO_4$ in the product for complete recovery of the sulfur formed by a stoichiometric reaction. The actual recovery of elemental sulfur was 43 to 85 pct of the theoretical recovery for most tests. Low recoveries of sulfur (40 to 60 pct) occurred in tests in which the temperature of the settling reactor was maintained at 175° C; recoveries of sulfur increased to 80 to 85 pct in test 10 when the settling reactor was operated at 160° C.

Losses of sulfur from the product came from three sources: (1) Less than 2 pct was lost as sulfur gases owing to undesired reactions; (2) sulfur vapors from the hot reaction mixtures condensed on colder surfaces; and (3) sulfur floated in the settling reactor and was removed with the overflow acid. The amount of sulfur lost with the overflow acid was high when the settling reactor was operated at 175° C, but was reduced to nearly negligible amounts at 160° C. This occurred because of the drastic change in the viscosity of liquid sulfur as it undergoes a molecular transformation from sulfur lambda (S_8) at 160° C to sulfur mu (S_4) at higher temperatures. This transformation causes the viscosity of the sulfur to increase from 228 mp (millipoise) at 160° C to 45,000 mp at 171° C. The effect of the high sulfur viscosity at the higher settling reactor temperatures was to cause the sulfur to float and to be removed with the overflow acid owing to gas entrapment. Reduction of the settling reactor operating temperature to 160° C reduced the viscosity of the sulfur and allowed the unhindered release of these small amounts of generated gases. Small amounts of gases were generated in the reaction mixture from two sources: Unstable boiling of the water reaction product, and oxidation of the sulfur by oxygen to produce sulfur dioxide gas.

Leaching and Crystallization of Zinc Sulfate

Limited supplies of the reaction products from the PRU reactor system allowed only limited tests of the PRU separation process because of the large in-process material inventories required by the system.

Filtration tests conducted on the reaction product slurry in the vacuum pan filter showed that, with operation at 29 inches of vacuum, the excess acid was readily removed from the slurry. The H_2SO_4 content of the slurry was reduced to an average of 10 pct with a 5-min filtration time, and a filter cake 1-1/2 to 2 inches thick was generated. No precoating of filters was needed to produce a clear filtrate.

The filter cake from the filter was leached batchwise in the four-stage countercurrent decantation leaching system with acid solutions of varying concentrations. It was not possible to maintain elevated solution temperatures for the duration of the leaching by mixing and settling, and recaking of the solids and recrystallization of the leach solution hampered the tests. Up to 48 hr was required to obtain good settling of the insoluble solids. The leach solution from the last stage was filtered through a cartridge polishing filter to remove residual suspended material. An analysis of the leach residue obtained from the leaching tests is given in table 5. The zinc separation was not as complete as in the laboratory leaching tests on reaction product samples because the bulk sample used in the PRU leaching tests included much unreacted ZnS resulting from start-ups and other operating transients not representative of steady-state PRU operation.

TABLE 5. - Analysis of potentially hazardous leach residue, wt-pct

Total sulfur	83.9
Elemental sulfur	78.6
Zinc	4.2
Lead	3.2
Iron	1.2
Copper	.3

The crystallizer was operated at -15° C using leach solution feed of two

different acid concentrations. Tests were also made with continuous feed of the leach solution and with batchwise conditions. The analysis of the feed and crystal liquor solutions is given in table 6. Large quantities of fine $ZnSO_4$ crystals formed. A dense slurry settled in the accumulator tank and was removed from the bottom. The crystals were free flowing and did not cake on any equipment, nor accumulate in the refrigeration tank of the crystallizer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the crystals confirmed that they were nearly identical to pure $ZnSO_4 \cdot 7H_2O$ crystals.

TABLE 6. - Concentration of crystallizer solutions, g/l

Constituent	Strong acid test		Weak acid test	
	Feed	Liquor	Feed	Liquor
H_2SO_4.....	366	517	245	301
Zinc.....	111.8	24.3	126.9	35.5
Iron.....	1.40	.53	2.33	.78
Cadmium.....	.52	.49	.57	.64
Copper.....	.49	.18	.19	.19

The crystal slurry retained a considerable amount of barren sulfuric acid liquor. All attempts to wash the crystals by elution failed because of the fineness of the crystals and because of packing. Digestion of the crystallizer solutions for up to 48 hr and variation of crystallizer conditions did not cause the crystals to increase in size. Large crystals (up to 1/2 inch) could be obtained from the strong acid slurry when the slurry was allowed to warm to ambient temperature for several days. TGA analysis of these crystals showed that they were $ZnSO_4 \cdot 6H_2O$ formed after dissolution of the $ZnSO_4 \cdot 7H_2O$ crystals.

Figure 6 is a plot of equilibrium solubility data for $ZnSO_4$ in H_2SO_4 solutions (10). Plotting the solubility data on the basis of weight ratios with H_2SO_4 has been found quite useful in the design of optimum crystallizer operation when two components (such as H_2O and $ZnSO_4$) are simultaneously crystallized from the feed liquor. Crystallization paths are shown as straight lines that cross lines representing varying acid concentrations.

Projections to Larger Scale Operation

The necessity to cool the overflow acid from the settling reactor before recycling created handling difficulties with the solidified liquid sulfur that would not exist in a large-scale operation where porcelain pumps designed to transfer the hot sulfuric acid would be available. Recycling of hot acid would also improve the energy efficiency of the process by decreasing the amount of heat required for acid reheat by a factor

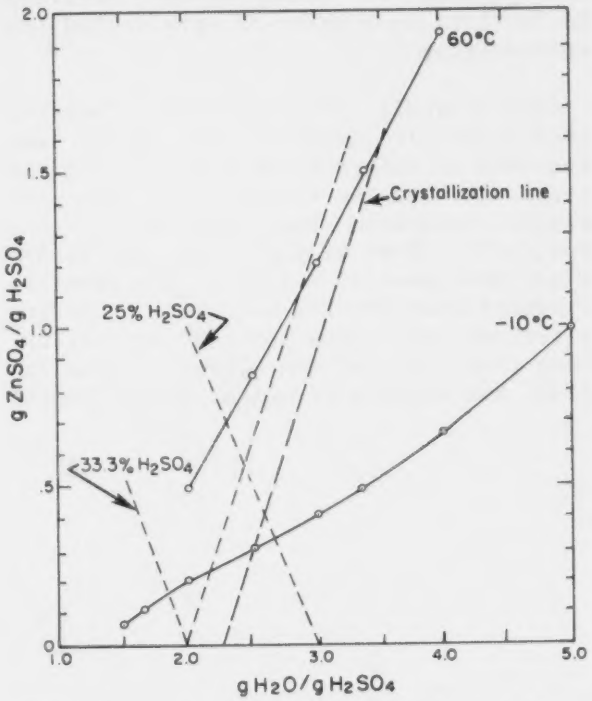

FIGURE 6. - Solubility of zinc sulfate in sulfuric acid solutions and crystallization lines for zinc sulfate heptahydrate formation.

of 3 to 5 from that used in these tests. In turn, this added capacity would provide the needed improved ratio of H_2SO_4 to ZnS feed in the stirred reactor.

Increased depth of the settling reactor would result from large-scale plant design. This would cause the product slurry to compact more, reducing the content of sulfuric acid while providing a larger fraction of overflow acid for recycle. This would further benefit process efficiency.

Increased process scale would also improve sulfur recovery. Sulfur losses that occur from formation of sulfur gases and from vaporization of liquid sulfur would both be reduced. Hydrogen sulfide gas formed in the stirred reactor is converted to elemental sulfur in proportion to the depth of the stirred reactor, and sulfur dioxide gas formed from contact of liquid sulfur at the surface with oxygen. The amount of sulfur vaporized from the surface of the reactors should be reduced from the mathematical relationship of exposed surface areas to reactor volumes.

SUMMARY

A three-stage glass PRU was designed and constructed to minimize sulfur gas evolution and to obtain maximum recovery of elemental sulfur and zinc sulfate from the reaction of ZnS concentrate with 80 pct H_2SO_4 at 170° to 190° C. The PRU was operated at steady-state conditions to react up to 9 kg/hr of preleached ZnS concentrate.

Approximately four to five times the stoichiometric quantity of H_2SO_4 was required to maintain the fluidity of the reactants, and the excess H_2SO_4 was partially separated and recycled to the reactors. Most of the sulfur was recovered as elemental sulfur. The reaction products were leached with water, leaving a residue containing about 80 pct sulfur. Less than 2 pct of the sulfur in the ZnS feed was evolved as sulfur gases in all tests. Up to 99.9 pct of the zinc was converted to soluble zinc sulfate.

The reaction products of the PRU reactor were further tested in a PRU separation circuit to produce neutral zinc sulfate usable as a feed material in conventional zinc electrolysis. The product was readily filtered by vacuum filtration to remove excess concentrated acid, and soluble zinc sulfate was leached from the solids with simulated zinc electrolysis solution. High yields of zinc sulfate heptahydrate crystals ($ZnSO_4 \cdot 7H_2O$) were obtained from the leach solution by batchwise and continuous crystallization at -15° C. The sulfuric acid in the barren crystal liquor was simultaneously concentrated by the removal of hydrate water in the crystals.

REFERENCES

1. Cammarota, V. A., Jr. Zinc. BuMines Minerals Yearbook 1980, v. 1, 1981, pp. 883-912.

2. Dewing, H. H., and A. A. Cochran. Sulfuric Acid Extraction Technique for Recovering Zinc and Sulfur From Sphalerite. BuMines RI 8322, 1978, 14 pp.

3. Downęs, K. W., and R. W. Bruce. The Recovery of Elemental Sulfur From Pyrite and Pyrrhotite. Trans. Can. Inst. Min. and Met., v. 58, 1955, pp. 127-132.

4. Forward, F. A., and J. Halpern. Hydrometallurgical Processes at High Pressures. Trans. Inst. Min. and Met., v. 66, 1956-57, pp. 181-189.

5. Forward, F. A., and H. Veitman. Direct Leaching Zinc-Sulfide Concentrates. J. Metals, v. 11, 1959, pp. 836-840.

6. McKay, D. R., and J. Halpern. A Kinetic Study of the Oxidation of Pyrite in Aqueous Suspension. Trans. AIME, v. 211, pp. 301-310.

7. McMahon, A. D., C. H. Cotterill, J. T. Dunham, and W. L. Rice. The U.S. Zinc Industry: A Historical Perspective. BuMines IC 8629, 1974, 76 pp.

8. Stanczyk, M. H., and C. Rampacek. Dissolution of Zinc From Sphalerite at Elevated Temperatures and Pressures. BuMines RI 5848, 1961, 23 pp.

9. Wedow, H., T. H. Kulsgaard, A. V. Heyl, and R. B. Hall. Zinc. Ch. in U.S. Mineral Resources. U.S. Geol. Survey Prof. Paper 820, 1973, pp. 697-711.

10. Seidel, A. Solubilities of Inorganic and Metal Organic Compounds. D. Van Nostrand Co., New York, v. 1, 3d ed., 1940, p. 1594.

APPENDIX.--PROCEDURE FOR RAPID IN-PLANT ASSAY OF SULFURIC ACID SOLUTIONS

Equipment

500-ml volumetric flask.

50-ml volumetric flask.

100-ml graduated cylinder.

800-ml beaker.

Small magnetic stirrer and stirrer bar.

Fast-response thermistor with digital readout.

Graph of acid concentration versus temperature increase (fig. A-1).

Procedure

1. Add 500 ml of water to the 800-ml beaker.

2. Fill 100-ml graduated cylinder with water and add 50 ml of H_2O to beaker.

3. Place beaker on magnetic stirrer and read temperature.

4. Obtain a 50-ml sample of acid in the 50-ml volumetric flask. Read temperature.

5. Rapidly add acid sample to water with magnetic stirrer operating. Rapidly rinse the acid sample from the volumetric flask with the remaining water in the graduated cylinder.

6. Read the temperature of the solution as soon as possible after it is mixed. Correct observed temperature for acid sample temperature by subtracting 1/17° C for each degree of acid sample over-temperature.

7. Use graph to determine acid concentration from corrected temperature increase of the solution.

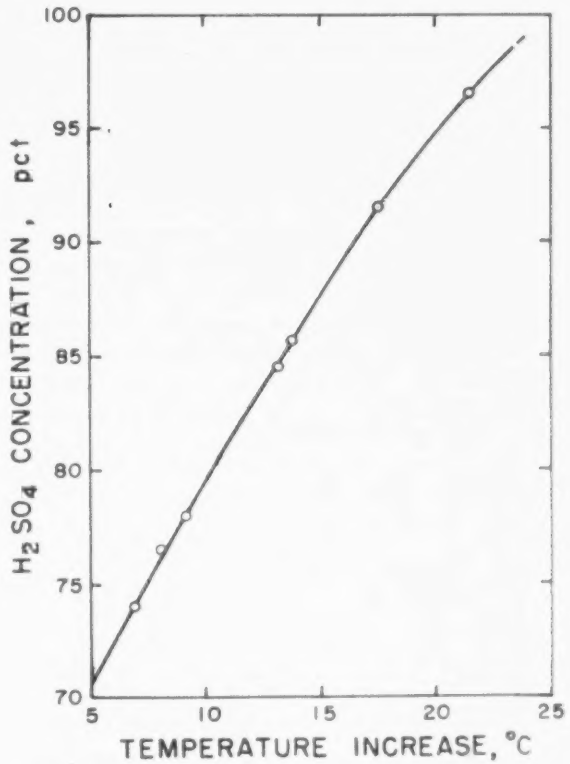

FIGURE A-1. - Determination of H_2SO_4 concentration by in-plant assay method.

☆U.S. GOVERNMENT PRINTING OFFICE 1982 - 505 - 002/63

INT.-BU.OF MINES,PGH.,PA. 26241